

Student questions: SESE Students colloquium

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“Tracking the Initial Oxygenation of Earth’s Oceans Using Thallium and Molybdenum Isotopes”

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My (Chad’s) responses are in red below:

How do you measure evidence of 'whiffs' of oxygen reachign the atmosphere from Cyanobacteria ~4.0 b.y.o?

One example of evidence for O₂ reaching early-Earth’s atmosphere is anomalously high molybdenum (Mo) enrichments in ancient marine sedimentary rocks that are 2.5 billion-years-old. Mo is highly insoluble in the absence of atmospheric O₂, but highly soluble in the presence of atmospheric O₂. In short, in order to mobilize such large quantities of Mo to the ocean where it could then accumulate in marine sediments, O₂ was likely to have been required at least in small amounts in the atmosphere.

What other locations in the world besides Australia can you find pristine samples of marine sediment to test isotopes?

There are “pristine” marine sedimentary rocks of various ages found throughout the world. However, when it comes to very old examples (i.e., older than 2.5 billion years old), there are two primary locations: Western Australia and South Africa.

The axis were missing on the graph; what do these axis represent for the given data?

I can’t seem to find in my slide deck the figure in question. My apologies if an axis on one of my figures was not clear!

I am not sure if I missed it or not but why specifically was Mo and Ti chosen when there could have been other elements that could have been chosen such as CO₂?

Molybdenum and thallium were chosen specifically because their isotopic abundances are known to be sensitive to Mn oxide burial. My co-authors and I wanted to test a hypothesis specifically concerning Mn oxide burial.

What changed to cause the great oxidation event?

That's a great question, one that we don't quite yet know the answer to! One plausible answer is that there was a shift in the balance of reductants at Earth's surface across the Great Oxidation Event (GOE). O_2 was likely being produced long before the GOE, but could not accumulate to appreciable amounts in Earth's atmosphere until the power of reductants at Earth's surface diminished (e.g., the chemistry and/or type of volcanism may have changed).

Why do we only have shale with evidence of the oxygen whiffs in that one location in Australia?

Actually, evidence for a "whiff" of O_2 at Earth's surface 2.5 billion years ago has also been found in sedimentary rocks from South Africa. It is difficult to correlate in time these two sets of rocks, but there is reason to think that they may capture evidence for the same "whiff" event.

Why do MnO_2 nodules preferentially incorporate light isotopes of molybdenum? Don't heavy isotopes always prefer to go into the lowest entropy phase, which I would expect to mean crystallizing out from seawater into the solid nodules?

The short answer is that the bonding environment for Mo is stronger in its seawater phase (MoO_4^{2-}) than it is on the surface of Mn oxide minerals. Heavier-mass isotopes always prefer stronger bonding environments. Through equilibrium exchange of Mo between these two phases, seawater (stronger bonding environment) gets enriched in heavier-mass Mo isotopes, and Mn oxides (weaker bonding environment) get enriched in lighter-mass Mo isotopes.

How do you know there aren't phases that would precipitate out of a reduced, oxygen-poor ocean that would incorporate heavy Tl and light Mo isotopes like MnO_2 nodules do, producing the same apparent isotope fractionations in seawater?

Great question! There are a few other known mechanisms that preferentially remove lighter-mass Mo isotopes from seawater (e.g., Fe oxides, thio-complexes, and organic matter). However, there is no known mechanism other than Mn oxides that are known to preferentially remove the heavier-mass Tl isotope from seawater. This is why pairing the two isotope systems is so powerful!

I wonder if he has compared the shifts in Mo and Tl systems to well documented oxygen isotope dating of major climatic shifts represented by the oxygen isotope system as found in fossil sea life such as foraminifera .

Unfortunately, foraminifera were probably not around during the Archean. Moreover, nobody has yet developed the methodology to measure Tl isotopes in forams. Someday!

Are you going to expand the locations of where you pull your core samples from to get a broader scope of the "fingerprint" or does matter?

Yes! There are some time-correlative black shales from South Africa that are particularly attractive, and cores that intersect them have already been drilled. Stay tuned!

Is there a reason why you specifically chose to use Mo and Tl isotopes?

Molybdenum and thallium were chosen specifically because their isotopic abundances are known to be sensitive to Mn oxide burial. My co-authors and I wanted to test a hypothesis specifically concerning Mn oxide burial.

What can initial oxygenation of the ocean tell us about our ocean today, and what can we do with that information?

We typically do things in the opposite manner: we learn things about how the modern ocean works, and then look for evidence of these things at times in Earth's past. ‘

One particularly cool thing that we have learned by investigating Earth's past ocean oxygenation is what processes may be or may have been operating on planets outside of our own. For example, even if we don't find an O₂ biosignature in an exoplanet's atmosphere, that does not mean that O₂ is not being produced or accumulating within the ocean on that planet. As was the case on ancient Earth, small amounts of O₂ could have accumulated in the ocean and could evade atmospheric detection.

Today's ocean have light Tl and heavy Mo; Mn nodules have the opposite values. How do you explain the contrast?

The former is a direct consequence of the latter. The seawater Tl and Mo isotope signatures today are light and heavy, respectively, because Mn oxides (which constitute nodules and crusts, etc.) are ubiquitous on the seafloor and preferentially remove heavier-mass Tl and lighter-mass Mo isotopes.